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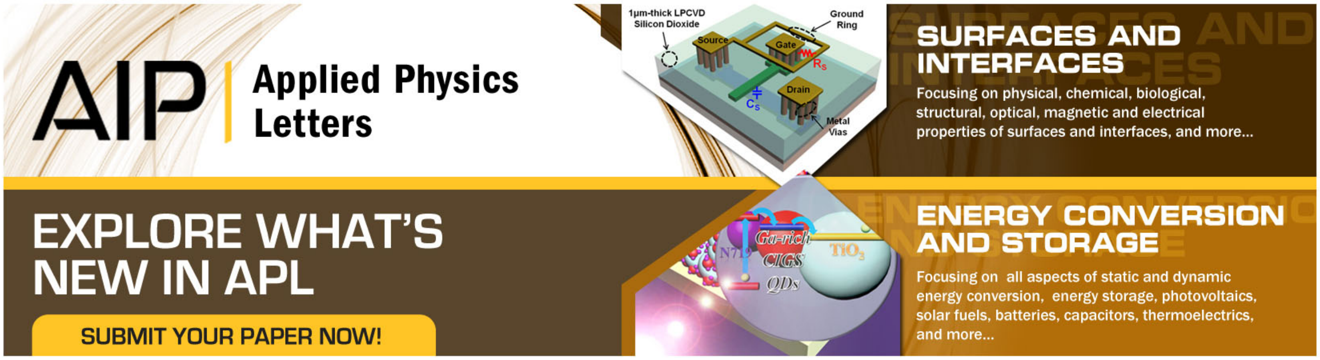

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Electric field-induced tetragonal to orthorhombic phase transitions in $[110]_c$-oriented $BaTiO_3$ single crystals

D. J. Franzbach,[1,2,a)] Y. J. Gu,[3] L. Q. Chen,[3] and K. G. Webber[1]
[1]*Institute of Materials Science, Technische Universität Darmstadt, 64287 Darmstadt, Germany*
[2]*Graduate School of Computational Engineering, Technische Universität Darmstadt, Darmstadt 64287, Germany*
[3]*Department of Materials Science and Engineering, Pennsylvania State University, University, Park, Pennsylvania 16802, USA*

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Electric field-induced phase transitions in $[110]_c$-oriented $BaTiO_3$ single crystals were studied by macroscopic electrical measurements in the temperature range from 20 °C to 50 °C. Discontinuous, hysteretic jumps in the polarization and strain were observed, indicating a tetragonal ↔ orthorhombic phase transition. The critical electric field to induce the transition was found to shift to higher values with increasing temperature. The Landau-Devonshire theory was used to analyze the observed electric field-induced T ↔ O phase transitions. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4769368]

Ferroelectric single crystals are widely utilized in sensing and transducing applications due to their superior electromechanical coupling along certain crystallographic axes.[1] In particular, single crystal relaxor ferroelectrics, such as $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ and $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$,[2,3] have been extensively investigated due to their excellent piezoelectric properties, electromechanical coupling, and unipolar strain capabilities that far exceed polycrystalline $Pb(Ti,Zr)O_3$.[4] In addition, relaxor ferroelectric single crystals have also been found to display phase transitions during the application of large electrical[2,5] and mechanical[5,6] loading, resulting in a nonlinear jump in polarization and strain. This has been supported by *in situ* XRD that has shown that the macroscopic strain corresponds directly to the microscopic strains in the crystal lattice.[7] The exact polarization rotation path is defined by the crystallographic orientation of the external field and is believed to be via a bridging monoclinic phase.[8] Field-induced phase transitions have also been observed in normal ferroelectrics,[9] which makes these phenomena of interest for numerous applications, such as thin films, where in-plane strains have been shown to shift the Curie temperature of perovskites by hundreds of degrees[10,11] and electromechanical energy harvesting through an Oleson cycle.[12] In addition, cutting edge polycrystalline lead-free ferroelectric materials display an exceptional unipolar strain during electric field loading, which is understood to be due to a temperature-dependent field-induced phase transition between the macroscopic nonpolar (ergodic relaxor) and a macroscopic polar (ferroelectric) order.[13] Some of the most promising candidates to replace $Pb(Ti,Zr)O_3$ are based on solid solutions of $(Bi_{1/2}Na_{1/2})TiO_3$ and $BaTiO_3$ doped with $(K_{0.5}Na_{0.5})NbO_3$ to moderate the nonpolar → polar phase transition.[14]

Various authors have used the phenomenological Landau-Devonshire (LD) theory to thermodynamically describe the stable phase in ferroelectric materials under combined thermal, electrical, and mechanical loads[10,15–20] as well as simulate the evolution of ferroelectric domain structures in response to external fields and defects.[21] In addition, Bell has demonstrated that the macroscopic electric field-induced rhombohedral ↔ tetragonal (R ↔ T) phase transition behavior of $Pb(Ti,Zr)O_3$ (Ref. 22) as well as the T → O → R phase transition sequence observed in $BaTiO_3$ single crystals can be predicted using LD.[16] Recently, Franzbach *et al.*[23] has shown using LD theory that electric field-induced tetragonal ↔ orthorhombic (T ↔ O) phase transitions along the $\langle 110\rangle_c$ crystallographic orientation are possible in tetragonal perovskites, e.g., $BaTiO_3$, although this transition has not been to date experimentally observed in $BaTiO_3$. The critical transformation electric field as well as the shape of the macroscopic hysteresis was found to significantly depend on the selected higher order dielectric stiffness coefficients.

Despite the excellent electromechanical properties of relaxor ferroelectrics, the description of these materials with a phenomenological LD theory is complicated by the transition from short- and long-range order with increasing $PbTiO_3$ content[24] and compositional heterogeneity[25] as well as random fields.[26] $BaTiO_3$ as a model of ferroelectric material with perovskite structure has been widely investigated experimentally and theoretically. Numerous investigators have proposed Landau coefficients for $BaTiO_3$.[17–20] Initial work described the Gibbs free energy of $BaTiO_3$ with a 6th-order expansion in terms of polarization without consideration for the possible temperature- or field-dependence of the higher order dielectric stiffness coefficients.[17] This 6th-order representation contained three coefficients that are linearly dependent on the temperature, which was found to accurately reproduce many of the structural and ferroelectric properties of single crystal $BaTiO_3$ as well as the phase transformation temperatures. The free energy function has since been extended to include temperature- and stress-dependence.[19,20] More recently, there has been a discussion whether an 8th-order expansion in polarization is required to fully capture the high temperature paraelectric ↔ ferroelectric phase transition behavior in response to an electric field.[19] First principle calculations suggest a much more complicated dependence of the different Landau coefficients

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[a] Electronic mail: franzb@ceramics.tu-darmstadt.de.

on temperature for a 6th-order than an 8th-order representation;[27] measurements of $BaTiO_3$ thin films under biaxial compressive strains of more than 1% due to substrate constraints showed a ferroelectric phase transition, which is not predicted with the 6th-order Landau description.[11] To capture this observed behavior, the Landau polynomial was expanded to the 8th-order, resulting in temperature-dependence for only the quadratic Landau coefficient.[18] Later work aimed to improve the representation of the low temperature phase transition, especially under compressive strain, in $BaTiO_3$ thin films by incorporating a stress- and temperature-dependence of various Landau coefficients.[20]

Despite the importance of perovskite materials in ferroelectric devices, e.g., thin films, and the number of investigations that have used LD theory to predict the stable phases, there have not been to date any studies that have directly compared macroscopic field-induced phase transition behavior below the Curie temperature to theory. Such studies would help to understand the importance of higher order Landau coefficients and their dependence on external fields, in addition to highlight the difficulties in extending a LD formulation to experimental conditions that may deviate significantly from those where the Landau coefficients were derived. To that end, here we report on the macroscopic temperature-dependent polarization and strain behavior of tetragonal $BaTiO_3$ single crystals that are electrically loaded along the $[110]_c$ crystallographic orientation. Experimental measurements are directly compared to LD theory.

Experiments were performed on commercial single domain BT single crystals (CrysTec GmbH) with a sample size of 2 mm × 2 mm × 1 mm, where the 1 mm thickness direction corresponded to the $[110]_c$ crystallographic orientation. Each 2 mm × 2 mm surface was sputtered with a silver electrode. The polarization for a triangular wave, unipolar electrical load was measured using a Sawyer-Tower arrangement at a frequency of 1 Hz. The strain was measured in the direction of the external field with a linear variable differential transformer arrangement. The sample was located in an oil bath to control the temperature during measurement (± 1 °C accuracy).

The measured polarization and strain at various temperatures between 20 °C and 50 °C are shown in Fig. 1. It is important to note here that the polarization represents the change in polarization from the remanent state during electrical loading; the crystal was supplied in a single domain state, which was taken as the reference polarization. Initially, the sample shows a nearly linear response to an increase in the external electrical load. This was expected as there was no driving force for ferroelectric domain switching in a single domain tetragonal $[110]_c$-oriented single crystal. It is likely that the increase in polarization and strain is due to the polarization rotation.[22,28] When the field is further increased, a discontinuous jump in both the polarization and strain can be observed. This feature can be explained by a field induced phase transition, where the polarization direction is rotated from the initial T $[100]_c$ to the O $[110]_c$ direction. Following this phase transition, the sample again shows an approximately linear response to the increasing field. Here, however, there is a change in the slope; the linear response in the T phase is steeper than in the O phase. When the electrical field is removed, the polarization of the sample linearly decreases until a reverse phase transition back to the original ferroelectric T phase is observed, resulting in the development of hysteresis. The critical electric fields for the T ↔ O transition for both forward and reverse transformation processes increased with temperature, which corresponds to a decrease in the size of the observed hysteresis and a change of the hysteresis shape to a more continuous transition. There is also an apparent decrease in the jump in polarization and strain during the phase transition with increasing temperature, e.g., at 20 °C the polarization increases by $0.06\,C/m^2$ during the T → O transition, while at 40 °C this is reduced to $\sim 0.02\,C/m^2$. Polarization and strain measurements display similar behavior although at higher temperatures, the strain-electric field loops begin to display an open hysteretic behavior throughout the loading cycle. It is possible that this is partially due to sample degradation during testing at lower temperatures; the discontinuous jump in strain was found to be large enough to generate cracking and subsequent sample failure after approximately 10–20 loading cycles.

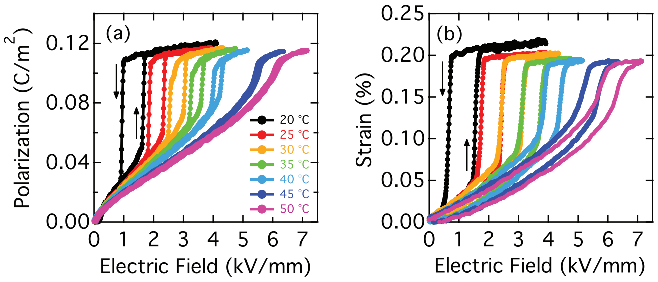

FIG. 1. Macroscopic polarization (a) and strain (b) of $[110]_c$-oriented $BaTiO_3$ single crystals during electric loading. Arrows indicate loading direction.

The observed macroscopic phase transition behavior was analyzed using the LD theory. It was assumed that the crystal was in a monodomain state under mechanical stress free boundary conditions, which was not strictly the case for the actual material after the first electrical cycle; it is expected that after the first electrical cycle a polydomain state is present. The polarization P of the sample was determined by minimizing the Gibbs free energy function for each electrical load step using the Landau coefficients provided by various investigators:[17–20]

$$\Delta G = \alpha_{ij}P_iP_j + \beta_{ijkl}P_iP_jP_kP_l + \gamma_{ijklmn}P_iP_jP_kP_lP_mP_n + \delta_{ijklmnop}P_iP_jP_kP_lP_mP_nP_oP_p - E_iP_i, \tag{1}$$

where α is the dielectric stiffness tensor and β, γ, and δ are the higher order stiffness coefficients. Previous work has shown that Eq. (1) results in an energy landscape that defines the stable polarization orientation as well as the electromechanical properties and polarization rotation path as a function of thermal, electrical, and mechanical fields.[29] It was found that all Landau potentials exhibited at global and local energy minima along the $\langle 100\rangle_c$ and $\langle 110\rangle_c$ directions in the considered temperature range, respectively. Calculations show that an electrical field in the $\langle 110\rangle_c$ direction resulted in a T → O phase transition. During unloading, however, a spontaneous reverse O → T phase transition was not found due to the absence of defects or thermal fluctuations in the model. This resulted in

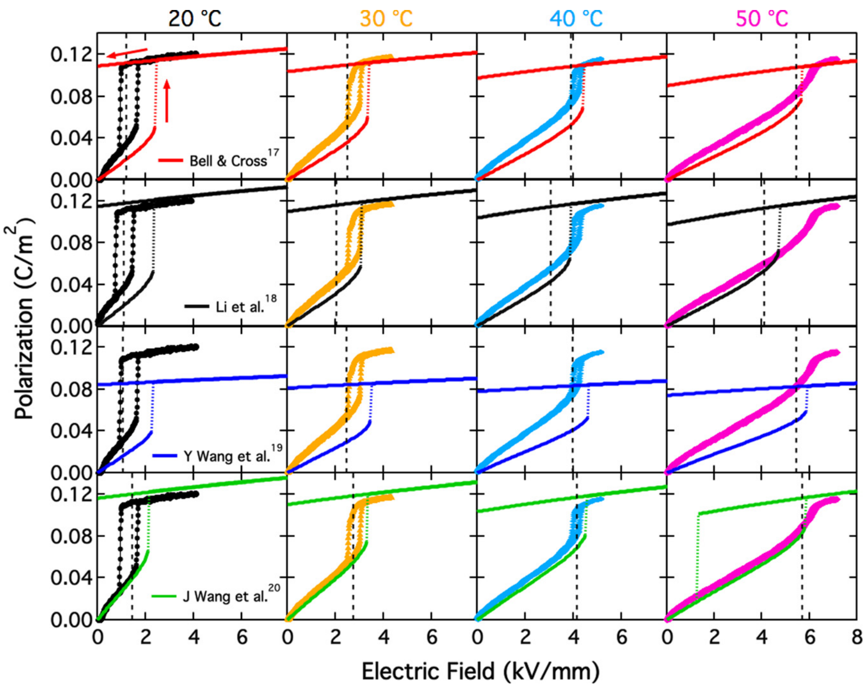

FIG. 2. Comparison of experimental data and calculations of the macroscopic polarization electric field behavior at various temperatures.[17–20] The black dashed lines indicate the equilibrium electric field E_0.

the prediction of larger hysteresis loops than experimentally observed. Calculations were performed for the same temperatures as in experiments. Figure 2 shows that comparison between experimental data and calculations using various 6th- and 8th-order expansions of the free energy,[17–20] with varying degrees of agreement. It is apparent that the T → O transition is predicted by each set of Landau coefficients, although the critical transition field, the jump in polarization during the transition, and the slope of the P-E curve in the T and O regime vary considerably. The equilibrium electric field E_0, which represents the electric field where the T and O phases have equivalent free energies, was also determined and shown in Figure 2 as a black dashed line. From all of the Landau coefficients considered, those of Wang *et al.*[20] have the best agreement with the experimental measurements. Typically, the dependence of α_1 on temperature is assumed to follow the Curie-Weiss law, resulting in a linear dependence on temperature.[4] However, following the work of Hayward and Salje,[30] Wang *et al.* has included a hyperbolic cotangent dependence of α_1 on temperature to include the influence of quantum effects.[20]

The temperature-dependence of the equilibrium electric field (Fig. 3(a)) and the linear material response in the T and O phases (Fig. 3(b)) have been calculated between 10 °C and 100 °C and compared to experimental data. The equilibrium electric field for the experimental measurements was taken as the average of the forward T → O and the reverse O → T transition fields. The calculated E_0 values were determined numerically, while an analytical solution for the relative reciprocal susceptibility can be determined for both the T and O phases by the second derivative of free energy function

$$\varepsilon = \frac{1}{\varepsilon_0}\vec{e}_0 \cdot \left(\frac{\partial^2 \Delta G}{\partial P_i \partial P_j}\right)^{-1} \cdot \vec{e}_0, \tag{2}$$

where ε_0 is the permittivity of free space and $\vec{e}_0$ is the unit vector along the crystallographic direction of interest. Equation (2) can then be solved to find the dependence of the relative permittivity in the $\langle 110 \rangle$-direction for the T phase

$$\varepsilon_T = \frac{1}{\varepsilon_0} \cdot \frac{2\alpha_1 + P_T^2(6\beta_{11} + \beta_{12} + (15\gamma_{111} + \gamma_{112})P_T^2 + (28\delta_{1111} + 28\delta_{1112})P_T^4)}{4(\alpha_1 + 6\beta_{11}P_T^2 + 15\gamma_{1111}P_T^4 + 28\delta_{1111}P_T^6)(\alpha_1 + \beta_{12}P_T^2 + \gamma_{112}P_T^4 + \delta_{1112}P_T^4)}, \tag{3}$$

where P_T is the spontaneous polarization of the tetragonal phase and α, β, γ, and δ are the Landau coefficients in reduced notation. It is apparent from Figure 3 that the equilibrium electric field for the T → O transition displays an approximately linear increase with temperature, which is in good agreement with all Landau coefficients except those from Li *et al.*[18] Accurate prediction of the phase transition fields, however, does not necessarily result in a better prediction of the macroscopic behavior. As shown in Figures ,3(a), the Landau coefficients proposed by Bell and Cross[17] and Wang *et al.*[19] are able to accurately capture the equilibrium electric field but are inaccurate in terms of linear material properties. The following conclusions can be drawn from the comparison of experimental measurements and simulations: (i) temperature dependence of the higher order Landau coefficients is not strictly necessary to match experimental

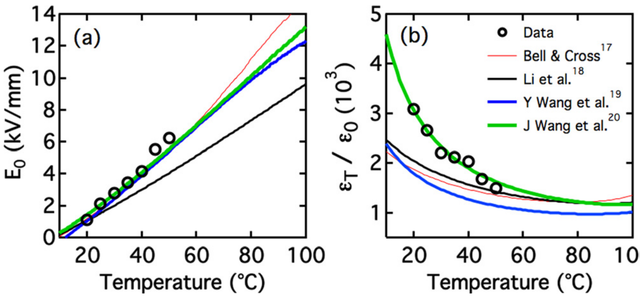

FIG. 3. Comparison of the measured equilibrium phase transition electric fields (a) and dielectric permittivity in the tetragonal phase (b) to thermodynamic calculations.

observations, if the temperature dependence of the first term is appropriately chosen; (ii) the temperature dependence of the quadratic Landau coefficient must not be linear, i.e., Curie-Weiss behavior, but can be a nonlinear function; (iii) it is important to consider field induced phase transitions when determining Landau coefficients, as they can be found in real materials; and (iv) care must be taken in extrapolating Landau coefficients derived from conditions that vary from the current constraints. The final point is of particular importance for phase field models, where local fields, for example elevated stresses found within a domain wall, may result in significantly different loading conditions then those where the Landau coefficients were originally derived.

Experimentally measured T → O phase transformations where analyzed by ferroelectric LD theory using various Landau coefficients. Comparisons of the slope of the P(E) loop in both phases and the temperature dependence of the equilibrium electrical field allows one to evaluate the accuracy of the various sets of Landau coefficients during off-axis electrical loading. These results have important applications for the prediction of the stable electric field- and stress-dependent phase in ferroelectric thin films and devices, where local electrical and mechanical fields can have a significant impact on device performance.

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